

## An Overview of Recent Organotin Studies in the Georgia Basin

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This paper examines changes in environmental indicators of tributyltin (TBT) and its decomposition products (dibutyltin, DBT; monobutyltin, MBT) since imposition of controlling regulations in 1989. Indicators include: 1. sediment and pore water concentrations; and 2. imposex occurrence and severity in neogastropod whelks. Data represent studies conducted in the Strait of Georgia, the west coast of Vancouver I., and three major contiguous harbors (Vancouver, Victoria, Esquimalt) since 1987 and features recent work since 2000.

It has been said that the tributyltin cation is probably the most toxic chemical that has ever been deliberately introduced into the aquatic environment (Maguire 2000). Indeed, it is one of the few man-made compounds for which there is a direct, well-established connection between it and its effects. Key sublethal effects include masculinization of neogastropod whelks, inhibition of growth and shell deformation in oysters, immunosuppression in flounder, and bioaccumulation in many aquatic species (for examples, see Shimasaki et al. 2003; Waldock et al. 1983; Salazar and Salazar 1987; Gibbs and Bryan 1986). Acute toxicity occurs at very low concentrations, often at low  $\text{ng.L}^{-1}$  concentrations.

In 1989, Canada, in concert with many other countries, introduced new regulations to control the use of TBT-based antifouling paints (CAPCO 1990). Under these controls, TBT-based paints were permitted on hulls greater than 25 meters long and maximum leach rates for permitted paints were required to be  $4 \mu\text{g.cm}^{-2}.\text{d}^{-1}$ . Over the past 16 years monitoring efforts have been focussed on changes in the specific environmental indicators of imposex in neogastropods and sediment loadings as a means of following the course of the expected decline in TBT concentrations.

Recently we have examined organotin concentrations at a number of marine disposal sites on two Canadian coasts. In the Strait of Georgia TBT surficial sediments (up to approx. 200 m depth) from the Point Grey (eight samples) and Sand Heads (four samples) near Vancouver were found to contain only TBT at near-detection quantities ( $1\text{--}2 \mu\text{g.kg}^{-1}$ ) at two sites.

Sediments from sites in three harbors (Vancouver, Victoria, and Esquimalt) collected in 2003 were found to contain TBT, DBT, and MBT in concentrations ranging from the detection limit to  $920 \mu\text{g.kg}^{-1}$ . Tributyltin accounted for 72–96% of the total butyltin loading in all three locations with the highest concentrations being related to proximity to shipyard activities. These values were comparable to box core data collected for these harbors in 1993 (Stewart and Thompson 1997). Overall, these results indicate that TBT decomposition is slow and/or that the input of new TBT has continued essentially unabated.

In the 2003 study, pore water samples from the harbor sediments were analyzed for butyltin content. Only TBT was determined in Vancouver Harbor samples at concentrations of  $0.1$  to  $0.3 \mu\text{g.L}^{-1}$  and values bore no relationship to bulk sediment loadings. Samples from Victoria and Esquimalt harbors contained TBT, DBT, and MBT in concentration ranges of  $0.1\text{--}2.8$ ,  $\text{nd}\text{--}0.4$  and  $0.6\text{--}6.1 \mu\text{g.L}^{-1}$  respectively. The percentage of the total as TBT ranged from 3.9 to 44  $\mu\text{g.L}^{-1}$ , again with no apparent relationship to the bulk levels. The apparent greater solubility and degradation of tributyltin could not be explained given the limited data; however there could be likely differences in the physico-chemical characteristics of the sediments and possibly the sources of the TBT. The degree of degradation in the Victoria and Esquimalt samples suggest a shorter half-life for TBT ( $T_{1/2}$ ) degradation. Previously we had calculated a value for  $T_{1/2}$  for the first order degradation in marina sediment to be approximately 8.7 y (Stewart and Thompson 1997). Half-lives for TBT degradation in the two phases may differ.

The appearance of male sex characteristics (growth of penis and *vas deferens*) in species (primarily of the genus *Nucella*) of neogastropod whelks has been used as a means of assessing TBT contamination for two decades. Assessment of the severity of TBT toxicity consists of measurement of penile size in female whelks relative to the male average (RPS). Calculation of the percentage of the incidence of imposex provides a measure of the extent and the course of any remediation. Data gathered previously by Ellis and co-workers had shown that imposex was at, or near, 100% in a number of species at most sites studied around Vancouver Island and the lower BC mainland (Vancouver area) in pre-control years (1987–89; see Tester et al 1996 and references therein). The RPS was greatest at sites nearest major shipping channels and harbors. By 1994 decreases in the incidence and RPS had been noted at many sites; however near Victoria and Vancouver harbors incidence remained essentially 100% while the RPS had decreased marginally. Our study of mostly Vancouver Island sites in 2000 (Reitsema et al. 2002) found further decreases in RPS and incidence. Incidence of 100% was found only at the Victoria Harbor breakwater. Concomitant decreases in RPS were also found at all sites.

While TBT concentrations remain high in harbor sediments and the occurrence and severity of imposex are showing some improvement, marine antifouling paints remain as the major source of the toxin on many ocean-going bottoms. In many countries with emerging economies little or no effort has been made to curb the use of these paints in spite of an International Maritime Organization (IMO) convention adopted in 2001 (IMO 2001). The Convention will enter into force 12 months after 25 states representing 25% of the world's merchant shipping tonnage have ratified it. It required a global prohibition on the application of organotin compounds in antifouling systems on ships by 1 January 2003, and a complete prohibition by the same date in 2008. To date, only 11 countries, representing just over 9% of the world's merchant tonnage, have ratified the convention. Neither the US nor Canada are among those that have ratified. Unless the major nations act soon (i.e. within the next 1-2 years), it is unlikely that the IMO convention will be effective in an absolute ban by 2008.

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